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(54) **Radiation curable compositions containing alkenyl ether functional polyisobutylenes**

(57) This invention provides radiation curable compositions comprising an alkenyl ether functional polyisobutylene, a cationic photoinitiator, a free radical photoinitiator and an alkenyl ether compound which is free of isobutylene units. The radiation curable compositions can further comprise an alkylphenol. This inven-

tion also relates to hydrocarbon silicone alkenyl ether compounds. The radiation curable compositions exhibit a low cure energy, have a high moisture vapor barrier, high damping characteristics, a high refractive index and provide a barrier to corrosive vapors while maintaining or enhancing modulus, tensile strength and toughness.

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Description

[0001] Our invention provides radiation curable compositions comprising an alkenyl ether functional polyisobutylene, a cationic photoinitiator, a free radical photoinitiator, and optionally an alkenyl ether compound which is free of isobutylene units. The radiation curable compositions can also further comprise an alkylphenol.

[0002] Polyisobutylenes (PIB) containing functional groups which are radiation curable have been disclosed in the art. For example, T. P. Liao and J.P. Kennedy in Polymer Bulletin, V. 6, pp. 135-141 (1981) disclose acryl and methacryl telechelic polyisobutylenes having the formula $\text{CH}_2=\text{C}(\text{R})-\text{COO}-\text{PIB}-\text{OOC}-\text{C}(\text{R})=\text{CH}_2$ where R is -H or CH_3 . These materials were prepared by reacting alpha, omega dihydroxypolyisobutylene, $\text{HOCH}_2-\text{PIB}-\text{CH}_2\text{OH}$ and excess acryloyl or methacryloyl chloride. These prepolymers are useful in the synthesis of a variety of new composites containing a soft polyisobutylene segment.

[0003] J. P. Kennedy and B. Ivan in Polymer Material Science and Engineering, V. 58, p.866 (1988) disclose allyl telechelic linear and star-branched polyisobutylenes prepared by a convenient rapid one pot polymerization functionalization process. The polymerization step involved living polymerization of isobutylene by recently discovered mono- or multifunctional initiating systems followed by electrophilic functionalizations by allyl trimethylsilane in the presence of TiCl_4 . Characterization indicated quantitative end allylations. Subsequent quantitative derivations of the allyl termini yielded mono-, di- and tri-functional hydroxyl- and epoxy-telechelic polyisobutylenes which could be cured to rubbery networks.

[0004] J. P. Kennedy and B. Ivan in the Journal of Polymer Science, Part A, Polymer Chemistry, V. 28, p. 89 (1990) disclose mono-, di-ended linear and three-arm star allyl telechelic polyisobutylenes which are prepared by a rapid economical one-pot polymerization-functionalization process. The process involved the living polymerization of isobutylene by mono-, di- or tri-functional initiating systems, specifically by aliphatic and aromatic tertiaryester and -ether/ TiCl_4 combinations, followed by electrophilic functionalization of the living sites with allyl-trimethylsilane. Quantitative derivations of the allyl termini yielded mono-, di- and tri-epoxy and -hydroxy-telechelic polyisobutylenes. Strong rubbery networks were made by curing the epoxy-telechelic polyisobutylenes with triethylene tetramine and by reacting the hydroxy-telechelic polyisobutylenes with MDI.

[0005] N.A. Merrill, I.J. Gardner and V.L. Hughes in RadTech North America Proceedings, V. 1, pp. 77-85 (1992) disclose conjugated diene functional polyisobutylenes which have a high reactivity to both ultraviolet and electron beam radiation. These conjugated diene functional polyisobutylenes, alone or in a formulation, are useful in preparing pressure sensitive adhesives.

[0006] In PCT Publication WO 9104992 is disclosed a functionalized copolymer of isobutylene and a paramethylstyrene, wherein at least one type of functional group is attached to the para-methyl group of the paramethylstyrene, the copolymer having a substantially homogenous compositional distribution. The functionalized groups are exemplified by alkoxides, phenoxides, carboxylates, thiolates, thiopenolates, thioethers, thiocarboxylates, dithiocarboxylates, thioureas, dithiocarbamates, xanthanates, thiocyanates, silanes, halosilanes, malonates, cyanides, amides, amines, carbazoles, phthalimides, pyridine, maleimide, cyanates and phosphines.

[0007] In PCT Publication WO 9211295 is disclosed a radiation reactive functionalized polymer comprising an isolefin having 4 to 7 carbon atoms and a para-alkylstyrene, wherein a radiation reactive functional group is attached to the para-alkyl group of the para-alkylstyrene and discloses radiation curable pressure sensitive adhesives comprising the functionalized polymer and a tackifier. The radiation curable groups disclosed therein are thioxanthenes, acrylates, aldehydes, ketones and esters.

[0008] U.S. Patent 5,665,823 discloses a method for preparing an acrylic functional polyisobutylene polymer or copolymer, the method comprising reacting a polyisobutylene polymer or copolymer which contains at least one carbon-bonded silanol group in it molecule with a silane having both an acrylic-containing group and a silicon-bonded hydrolyzable group in its molecule.

[0009] Furthermore, radiation curable compositions which contain vinyl ether functional organosilicon compounds have also been described in the art. For example, U.S. Patent 4,617,238 discloses a photopolymerizable composition comprising (a) an organopolysiloxane having at least one Si-bonded vinyloxy functional group of the formula $\text{H}_2\text{C}=\text{CH}-\text{O}-\text{G}-$, where G is alkylene (such as propylene) or alkylene interrupted by at least one divalent heteroradical selected from -O-, divalent phenylene or substituted divalent phenylene, or combination of such heteroradicals, and (b) an onium salt catalyst. This patent also describes a method wherein the vinyl ether group is introduced into the organopolysiloxane by addition (hydrosilylation) of compounds with an allyl and a vinyl ether group to an SiH group of the organopolysiloxane in the presence of a platinum catalyst. Only the allyl group is added to the SiH group in this method, while the vinyl ether group is preserved and thus only one vinyl ether group for each SiH group can be incorporated into the siloxane molecule at any given time.

[0010] European Patent Publication 0462389 teaches thermosetting organopolysiloxanes with oxyalkylene vinyl ether groups bonded by SiOC groups and the vinyl groups may be substituted by alkyl groups. A method for the preparation of these compounds is also taught and their application as photochemically thermosetting polysiloxanes

in encapsulating compounds, as non-stick coating compounds for flat carriers or as modified additives in compounds which can be thermoset radically, cationically or by UV or electron radiation.

[0011] U.S. Patent 5,270,423 discloses organosilicon compounds with a siloxane portion of the general formula-OR'OC=CHR" linked via an SiOC bond wherein R' is a divalent hydrocarbon group and R" is hydrogen or an alkyl group which are useful in radiation curable compositions, in which they are mixed with an initiator. The compositions are particularly useful in UV radiation curable coatings.

[0012] U.S. Patent 5,594,042 discloses radiation curable compositions comprising vinyl ether functional siloxanes and aromatic iodonium salt or aromatic sulfonium salt photoinitiators which cure upon exposure to ultraviolet or electron beam radiation. The vinyl ether groups are linked to the silicon atom on the siloxane through an SiOC bond and the photoinitiators are disclosed as being preferably either diaryliodonium salts of sulfonic acids or triarylsulfonium salts of sulfonic acids.

[0013] U.S. Patent 5,629,095 discloses vinyl ether functional siloxane resins, radiation curable coating compositions comprising a vinyl ether functional siloxane resin and a photocleavable acid, and a coated article obtained by applying the radiation curable coating composition to a substrate and then exposing the coating to radiation in an amount sufficient to cure the coating. The vinyl ether group in the siloxane resin is attached to the silicone atom through an SiOC bond.

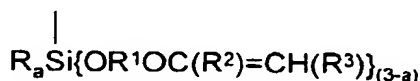
[0014] Our present invention provides radiation curable compositions comprising an alkenyl ether functional polyisobutylene, a cationic photoinitiator, a free radical photoinitiator, and optionally an alkenyl ether compound which is free of isobutylene units. The radiation curable compositions can also further comprise an alkylphenol.

[0015] This invention also relates to hydrocarbon silicone alkenyl ether compounds.

[0016] Our invention produces radiation curable compositions which exhibit a low cure energy, have a high moisture vapor barrier, high damping characteristics and a high refractive index. Furthermore, our invention produces radiation curable compositions which provide a barrier to corrosive vapors and have maintained or enhanced modulus, tensile strength and toughness.

[0017] This invention relates to a radiation curable composition comprising:

[0018] (A) an alkenyl ether-functional polyisobutylene polymer in which at least 50 mole percent of the non-terminal repeating units of the polymer are isobutylene units and containing at least one group having the formula



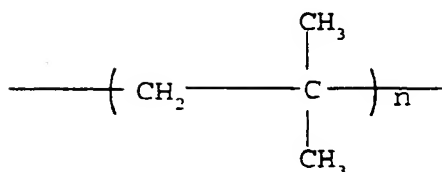
wherein R is independently selected from monovalent hydrocarbon groups or alkoxy groups, R¹ is a divalent hydrocarbon group having from 2 to 20 carbon atoms, R² and R³ are independently selected from a hydrogen atom or a monovalent hydrocarbon group, and a has a value of 0 to 2, (B) a cationic photoinitiator, and (C) a free radical photoinitiator.

[0019] The monovalent hydrocarbon groups of R are exemplified by alkyl groups such as methyl, ethyl, propyl, butyl, hexyl, octyl and decyl, aryl groups such as phenyl, tolyl and xylyl, and can also be any monovalent hydrocarbon group which has at least one of its hydrogen atoms replaced with a halogen, such as fluorine, chlorine or bromine, and these monovalent hydrocarbon groups are exemplified by CF₃CH₂CH₂- and C₄F₉CH₂CH₂-. The alkoxy groups are exemplified by methoxy, ethoxy, propoxy and butoxy. It is highly preferred that R is independently selected from methyl or methoxy. Each R group can be the same or different, as desired.

[0020] Divalent hydrocarbon groups suitable as R¹ are exemplified by alkylene groups such as ethylene, propylene, butylene, pentylene, trimethylene, 2-methyltrimethylene, pentamethylene, hexamethylene, 3-ethyl-hexamethylene, octamethylene, decamethylene, -(CH₂)₁₈- and cycloalkylene groups such as cyclohexylene, arylene groups such as phenylene. Examples of suitable divalent halohydrocarbon groups also include any divalent hydrocarbon group wherein one or more hydrogen atoms have been replaced by halogen, such as fluorine, chlorine or bromine exemplified by -CH₂CH₂CF₂CF₂CH₂CH₂-. Each R¹ can be the same or different as desired. Preferably R¹ is butylene.

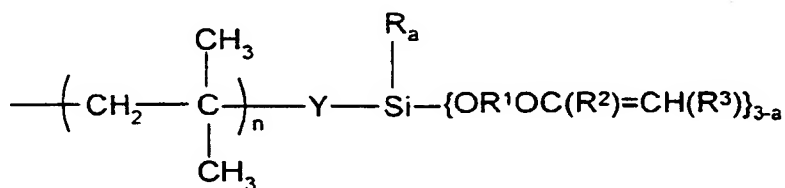
[0021] The groups R² and R³ are independently selected from a hydrogen atom or a monovalent hydrocarbon group exemplified by alkyl groups such as methyl, ethyl, propyl or butyl. The groups R² and R³ may be the same or different. Preferably R² and R³ are hydrogen atoms. In the formula above, it is preferred that a have a value of zero.

[0022] For the purposes of this invention, the backbone of the alkenyl ether functional polyisobutylene polymer may be any linear or branched polymer or copolymer wherein at least 50 mole percent, preferably at least 80 mole percent, of the repeat units are isobutylene units having the following structure:

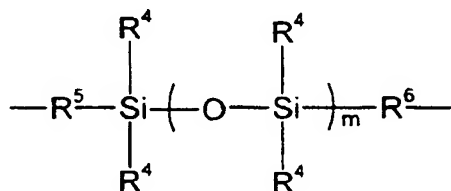


In the polymer or copolymer of the invention, the above described alkenyl ether group can be disposed either along the chain or at the terminals thereof, or any combination of the above. As used herein, the term "polymer" is generic to polymers, oligomers and copolymers, all of which are within the scope of this invention.

[0023] In a preferred embodiment of this invention, the alkenyl ether functional polyisobutylene polymer (A) is a polymer containing at least one group having the formula



wherein at least 50 mole percent of the non-terminal repeating units of the polymer are isobutylene units, R is independently selected from monovalent hydrocarbon groups or alkoxy groups, R¹ is a divalent hydrocarbon group having from 2 to 20 carbon atoms, R² and R³ are independently selected from a hydrogen atom or a monovalent hydrocarbon group, n has a value from 5 to 10,000, a has a value of 0 to 2, and Y is selected from (i) an alkylene group having from 2 to 10 carbon atoms or (ii) a group having the formula



wherein R⁴ is a monovalent hydrocarbon group, R⁵ and R⁶ are independently alkylene groups having from 2 to 10 carbon atoms and m is an integer having a value from 1 to 5.

[0024] The groups R and R¹ are as defined hereinabove, including preferred embodiments thereof. Preferably, R is independently selected from methyl or methoxy, and R¹ is butylene. Preferably, a has a value of 0 or 1.

[0025] The alkylene groups of Y(i) are exemplified by ethylene, propylene, butylene, pentylene, trimethylene, 2-methyltrimethylene, pentamethylene, hexamethylene, 3-ethylhexamethylene, octamethylene and decamethylene.

[0026] In the formula for Y(ii) above, the monovalent hydrocarbon groups of R⁴ are as described above for R and preferably R⁴ is methyl. The alkylene groups for R⁵ and R⁶ are as defined above for Y(i). Preferably, R⁵ and R⁶ are independently selected from ethylene and propylene. It is highly preferred that R⁵ is propylene and R⁶ is ethylene. It is also preferred that m has a value of 1.

[0027] It is preferred for purposes of this invention that from 10 to 100 weight percent of the alkenyl ether functional polyisobutylene polymer described above be used, and it is highly preferred that from 50 to 100 weight percent of this compound be employed, said weight percent being based on the total weight of the radiation curable composition.

[0028] Component (B) in the composition of this invention is cationic photoinitiator. Suitable cationic photoinitiators are selected from onium salts, diaryliodonium salts of sulfonic acids, triarylsulfonium salts of sulfonic acids, diaryliodonium salts of boronic acids or triarylsulfonium salts of boronic acids.

[0029] The onium salts are preferably selected from $R^7_2I^+MX_2^-$, $R^7_3S^+MX_2^-$, $R^7_3Se^+MX_2^-$, $R^7_4P^+MX_2^-$ or $R^7_4N^+MX_2^-$, wherein each R^7 is an organic group having from 1 to 30 carbon atoms exemplified by aromatic carbocyclic groups having from 6 to 20 carbon atoms. Each R^7 can be substituted with from 1 to 4 monovalent hydrocarbon groups exemplified by alkoxy groups having from 1 to 8 carbon atoms, alkyl groups having from 1 to 16 carbon atoms, nitro, chloro, bromo, cyano, carboxyl, mercapto and aromatic heterocyclic groups exemplified by pyridyl, thiophenyl and pyranyl. The symbol M in the formulae hereinabove are metals or metalloids which include transition metals exemplified by Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, Sc, V, Cr, Mn, Cs, rare earth metals exemplified by lanthanides, for example, Cd, Pr and Nd and metalloids exemplified by B, P and As. MX_2^- is a non-basic, non-nucleophilic anion exemplified by BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , $SbCl_6^-$, HSO_4^- , ClO_4^- , $FeCl_4^-$, $SnCl_6^-$ and $BiCl_5^-$.

[0030] Preferred onium salts are exemplified by bis-diaryl iodonium salts, for example, bis(dodecyl phenyl) iodonium hexafluoroarsenate, bis(dodecylphenyl) iodonium hexafluoroantimonate and dialkylphenyl iodonium hexafluoroantimonate.

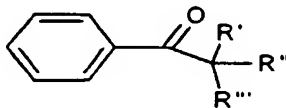
[0031] Diaryliodonium salts of sulfonic acids, triarylsulfonium salts of sulfonic acids, diaryliodonium salts of boronic acids and triarylsulfonium salts of boronic acids are also suitable as the cationic photoinitiator (B). Preferred diaryliodonium salts of sulfonic acid are diaryliodonium salts of perfluoroalkylsulfonic acids and diaryliodonium salts of aryl sulfonic acids. Preferred diaryliodonium salts of perfluoroalkylsulfonic acids are exemplified by diaryliodonium salts of perfluorobutanesulfonic acid, diaryliodonium salts of perfluoroethanesulfonic acid, diaryliodonium salts of perfluorooctanesulfonic acid and diaryliodonium salts of trifluoromethane sulfonic acid. Preferred diaryliodonium salts of aryl sulfonic acids are exemplified by diaryliodonium salts of para-toluene sulfonic acid, diaryliodonium salts of dodecylbenzene sulfonic acid, diaryliodonium salts of benzene sulfonic acid and diaryliodonium salts of 3-nitrobenzene sulfonic acid.

[0032] Preferred triarylsulfonium salts of sulfonic acid are triarylsulfonium salts of perfluoroalkylsulfonic acids and triarylsulfonium salts of aryl sulfonic acids. Preferred triarylsulfonium salts of perfluoroalkylsulfonic acids are exemplified by triarylsulfonium salts of perfluorobutanesulfonic acid, triarylsulfonium salts of perfluoroethanesulfonic acid, triarylsulfonium salts of perfluorooctanesulfonic acid and triarylsulfonium salts of trifluoromethane sulfonic acid. Preferred triarylsulfonium salts of aryl sulfonic acids are exemplified by triarylsulfonium salts of para-toluene sulfonic acid, triarylsulfonium salts of dodecylbenzene sulfonic acid, triarylsulfonium salts of benzene sulfonic acid and triarylsulfonium salts of 3-nitrobenzene sulfonic acid.

[0033] Preferred diaryliodonium salts of boronic acids and triarylsulfonium salts of boronic acids are compounds such as those disclosed in European Patent Application 0562922. Preferred diaryliodonium salts of boronic acids include diaryliodonium salts of perhaloarylboronic acids and preferred triarylsulfonium salts of boronic acids are the triarylsulfonium salts of perhaloarylboronic acid.

[0034] Preferably the amount of cationic photoinitiator (B) is from 0.01 to 5.0 weight percent based on the total weight of the composition, and it is highly preferred to use from 0.1 to 2.0 weight percent based on the total weight of the radiation curable composition.

[0035] Component (C) in the compositions of this invention is a free radical photoinitiator. The free radical photoinitiators of this invention can be any benzoin exemplified by benzoin alkyl ethers, benzophenone and its derivatives such as 4,4'-dimethyl-amino-benzophenone (Michler's Ketone), acetophenones exemplified by dialkoxyacetophenones, dichloroacetophenones and trichloroacetophenones, benzils exemplified by benzil ketals, quinones and O-acetylated- α -oximinoketones. Preferably the free radical photoinitiator is a compound having the formula

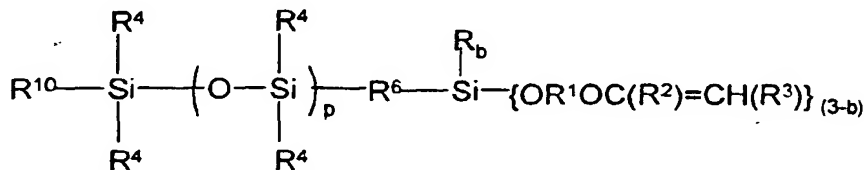


wherein R' is selected from -H, an alkoxy group and a halogen atom, R'' is selected from -OH, an alkoxy group and a halogen atom and R''' is selected from -H, an alkyl group and a halogen atom. Preferred embodiments of this compound are (i) where R' is -H, R'' is -OH and R''' is methyl or phenyl, (ii) where R' is -H, R'' is an alkoxy group and R''' is phenyl (for benzoin alkyl ethers), (iii) where both R' and R'' are alkoxy groups and R''' is phenyl (for benzil ketals), (iv) where both R' and R'' are alkoxy groups and R''' is -H (for dialkoxyacetophenones), and (v) where both R' and R'' are -Cl and R''' is -Cl or -H (for di- and trichloroacetophenones). It is especially preferred for the compositions that component (C) is Darocur® 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one).

[0036] Preferably the amount of free radical photoinitiator (C) is from 0.01 to 5.0 weight percent based on the total weight of the composition, and it is highly preferred to use from 0.1 to 2.0 weight percent based on the total weight of the radiation curable composition.

[0037] The compositions of this invention can further comprise (D) an alkenyl ether compound which is free of iso-

butylene units. Component (D) is exemplified by alkenyl ether compounds selected from (i) a vinyl ether compound having the formula $(\text{CH}_2=\text{CHOR}^8)_d\text{CR}^9_{4-d}$ wherein R^8 is a divalent hydrocarbon group having from 1 to 20 carbon atoms, R^9 is selected from a hydrogen atom and a monovalent hydrocarbon group having from 1 to 20 carbon atoms, and d has a value of 1 to 3, (ii) a hydrocarbon silicone alkenyl ether compound having the formula



wherein R^1 and R^6 are independently divalent hydrocarbon groups having from 1 to 20 carbon atoms, R^4 is a monovalent hydrocarbon group having from 1 to 20 carbon atoms, R^2 and R^3 are independently selected from a hydrogen atom and a monovalent hydrocarbon group, R^{10} is an alkyl group having from 8 to 16 carbon atoms, R is independently selected from R^4 or an alkoxy group, b has a value of 0 to 2, and p has a value of 0 to 1, or (iii) a long chain hydrocarbon silicone alkenyl ether compound having the formula



wherein R is independently selected from monovalent hydrocarbons having from 1 to 20 carbon atoms or an alkoxy group, R^{11} is an alkyl group having from 8 to 16 carbon atoms, R^2 and R^3 are independently selected from a hydrogen atom or a monovalent hydrocarbon groups, R^1 is a divalent hydrocarbon group having 1 to 20 carbon atom and c has a value of 0 to 2.

[0038] The monovalent and divalent hydrocarbon groups are as delineated above for the alkenyl ether functional polyisobutylene, including preferred embodiments thereof. In the formula for (i), preferably R^8 is an alkylene group having from 1 to 6 carbon atoms, preferably methylene, R^9 is an alkyl group having from 1 to 10 carbon atoms, preferably ethyl, and d has a value of 3.

[0039] In the formula for (ii), preferably R^1 and R^6 are independently alkylene groups having from 1 to 6 carbon atoms, preferably R^1 is butylene and R^6 is ethylene, R^4 is an alkyl group having from 1 to 10 carbon atoms, preferably methyl, R^{10} is exemplified by octyl ($-\text{C}_8\text{H}_{17}$), decyl ($-\text{C}_{10}\text{H}_{21}$), dodecyl ($-\text{C}_{12}\text{H}_{25}$), tetradecyl ($-\text{C}_{14}\text{H}_{29}$) and hexadecyl ($-\text{C}_{16}\text{H}_{33}$), with dodecyl and hexadecyl being preferred, R^2 and R^3 are independently selected from a hydrogen atom or a monovalent hydrocarbon group, preferably R^2 and R^3 are each hydrogen atoms, R is independently selected from the group consisting of methyl and methoxy, preferably b has a value of 0, and preferably p has a value of 0 or 1, preferably 1.

[0040] In the formula for (iii), preferably R^1 is an alkylene group having from 1 to 6 carbon atoms, preferably R^1 is butylene, R is independently selected from methyl and methoxy, R^{11} is exemplified by dodecyl ($-\text{C}_{12}\text{H}_{25}$), tetradecyl ($-\text{C}_{14}\text{H}_{29}$) and hexadecyl ($-\text{C}_{16}\text{H}_{33}$), with dodecyl and hexadecyl being preferred, R^2 and R^3 are independently selected from a hydrogen atom or a monovalent hydrocarbon group, preferably R^2 and R^3 are hydrogen atoms, and preferably c has a value of 0.

[0041] Preferably the amount of Component (D) is up to 70 weight percent based on the total weight of the composition, and it is highly preferred to use from 0 to 50 weight percent based on the total weight of the radiation curable composition.

[0042] The compositions of this invention can also further comprise (E) an alkylphenol having from 6 to 18 carbon atoms. The alkyl group is exemplified by hexyl ($-\text{C}_6\text{H}_{13}$), octyl ($-\text{C}_8\text{H}_{17}$), decyl ($-\text{C}_{10}\text{H}_{21}$), dodecyl ($-\text{C}_{12}\text{H}_{25}$), tetradecyl ($-\text{C}_{14}\text{H}_{29}$), hexadecyl ($-\text{C}_{16}\text{H}_{33}$) and octadecyl ($-\text{C}_{18}\text{H}_{37}$), with dodecyl being preferred. It is especially preferred that (E) is dodecylphenol. For the purposes of this invention, "dodecylphenol" denotes a compound having the formula $\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{OH}$ or a mixture comprising isomers of a compound having the formula $\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{OH}$.

[0043] Preferably the amount of dodecylphenol (E) is up to 5.0 parts by weight, and it is highly preferred to use from 0.5 to 2.0 parts by weight per 100 parts by weight of the radiation curable composition.

[0044] The radiation curable compositions of this invention can also contain ingredients exemplified by reinforcing and extending fillers such as treated silicas, hydrocarbon diluents such as linear alkyl dodecylbenzene and functional hydrocarbons such as C_{8-16} aliphatic glycidyl ethers, sensitizers such as 2-isopropylthioxanthone or benzophenone,

colorants, dyes, preservatives, fragrances, stabilizers and adhesion modifiers.

[0045] The radiation curable compositions of this invention can be prepared by mixing the materials described hereinabove and any optional components in any order, using any suitable mixing means, such as a spatula, a drum roller, a mechanical stirrer, a three-roll mill, a sigma blade mixer, a bread dough mixer or a two-roll mill.

[0046] This invention further relates to a method of making a radiation curable composition comprising (I) mixing components (A)-(C) and optionally (D) described hereinabove. The method can further comprise (II) adding (E) an alkylphenol having from 6 to 18 carbon atoms during step (I). Components (A)-(E) are as described above, including preferred embodiments and amounts thereof.

[0047] The present invention further relates to a method of making an article of manufacture comprising (I) applying a radiation curable composition comprising components (A)-(C) described hereinabove, to a solid substrate to form a coating, and (II) exposing the coating to an energy source selected from the group consisting of (i) ultraviolet light and (ii) visible light in an amount sufficient to cure the coating.

[0048] The composition of (I) can further comprise (D) an alkenyl ether compound which is free of isobutylene units, and (E) an alkylphenol having from 6 to 18 carbon atoms, and any of the optional ingredients recited above. Components (A)-(E) and the optional ingredients are as described above, including preferred embodiments and amounts thereof.

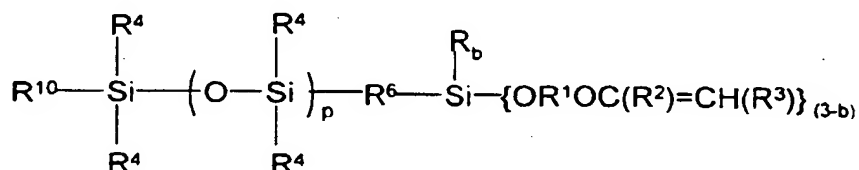
[0049] The coating may be applied by any suitable manner known in the art, such as by spreading, brushing, extruding, spraying, gravure, kiss-roll and air-knife.

[0050] The solid substrate can be a flexible sheet material such as paper, polyolefin film, polyolefin-coated paper, foil, wood, cardboard and cotton, metallic materials such as aluminum, copper, steel and silver, siliceous materials such as glass and stone and synthetic polymer materials such as polyolefins, polyamides, polyesters and polyacrylates. As to form, the solid substrate can be sheet-like, such as a peelable release liner for pressure sensitive adhesive, a fabric or a foil or a fiber or a three-dimensional in form.

[0051] Curing itself may be achieved in any of the known ways, including passing a coated substrate under the desired source of radiation, for example, a UV lamp, at a predetermined rate and exposing a completely coated substrate to radiation by switching on the required energy source for a predetermined time.

[0052] The radiation curable compositions are preferably cured in the form of films. The cured films are expected to have high refractive index, good barrier properties, good adhesion and good damping properties. It is preferable to apply these coatings to surfaces that are adversely affected by exposure to oxygen, moisture vapor and other environmental factors. The radiation curable coatings are particularly useful as high refractive index coatings for optical fibers. The application of the radiation curable compositions to optical fibers and curing of the compositions can be achieved by conventional equipment (see Blyler and Aloisio Polymers for Coating Optical Fibers, Chemtech, Nov. 1987, pages 680-684). The curable compositions can also be used as an additive to compositions to increase barrier properties. The radiation curable compositions can be used to increase the barrier properties of sealants and potting used for encapsulating electronic devices that are adversely affected by moisture.

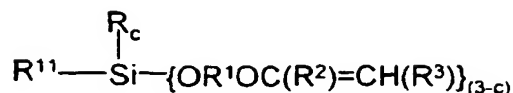
[0053] This invention also relates to a hydrocarbon silicone alkenyl ether compound having the formula



wherein R^1 and R^6 are divalent hydrocarbon groups having from 1 to 20 carbon atoms, R^4 is a monovalent hydrocarbon group having from 1 to 20 carbon atoms, R^{10} is an alkyl group having from 8 to 16 carbon atoms, R^2 and R^3 are independently selected from a hydrogen atom or a monovalent hydrocarbon group, R is independently selected from R^4 or an alkoxy group, b has a value of 0 to 2 and p has a value of 0 to 1.

[0054] Preferably R^1 and R^6 are alkylene groups having from 1 to 6 carbon atoms, preferably R^1 is butylene and R^6 is ethylene, R^4 is an alkyl group having from 1 to 10 carbon atoms, preferably methyl, R^2 and R^3 are independently selected from a hydrogen atom or a monovalent hydrocarbon groups, preferably R^2 and R^3 are each hydrogen atoms, R^{10} is exemplified by octyl ($-\text{C}_8\text{H}_{17}$), decyl ($-\text{C}_{10}\text{H}_{21}$), dodecyl ($-\text{C}_{12}\text{H}_{25}$), tetradecyl ($-\text{C}_{14}\text{H}_{29}$) and hexadecyl ($-\text{C}_{16}\text{H}_{33}$), with dodecyl and hexadecyl being preferred, R is independently selected from methyl or methoxy, preferably b has a value of 0, and preferably p has a value of 0 or 1, preferably 1.

[0055] This invention also relates to a hydrocarbon silicone alkenyl ether compound having the formula



wherein R is independently selected from a monovalent hydrocarbon group having from 1 to 20 carbon atoms and an alkoxy group, R² and R³ are independently selected from a hydrogen atom or a monovalent hydrocarbon group, R¹¹ is an alkyl group having from 8 to 16 carbon atoms, R¹ is a divalent hydrocarbon group having 1 to 20 carbon atom and c has a value of 0 to 2.

[0056] Preferably R¹ is an alkylene group having from 1 to 6 carbon atoms, preferably R¹ is butylene, R² and R³ are independently selected from a hydrogen atom or a monovalent hydrocarbon groups, preferably R² and R³ are each hydrogen atoms, R is independently selected from methyl or methoxy. R¹¹ is exemplified by dodecyl (-C₁₂H₂₅), tetradecyl (-C₁₄H₂₉) and hexadecyl (-C₁₆H₃₃), with dodecyl and hexadecyl being preferred, preferably c has a value of 0.

[0057] Materials: The allyl functional polyisobutylene (PIB) polymer was obtained from Kaneka Corporation as Epion™ 200A polymer. Hydroxybutyl vinyl ether, 1-hexadecene, methyltrichlorosilane and methyldichlorosilane was purchased from Aldrich Chemical Company, as were other solvents and common reagents used in the examples. Trimethylolpropane trivinyl ether was obtained from BASF Corporation. The platinum (vinylsiloxane) catalyst was prepared by the procedure of Hitchcock et. al., Angew. Chem. Int. Ed. Engl. 1991, 30. ¹³C and ²⁹Si nuclear magnetic resonance spectroscopy (NMR) was used to confirm the structures. Molecular weight of each polyisobutylene was determined by gel permeation chromatography using PIB standards.

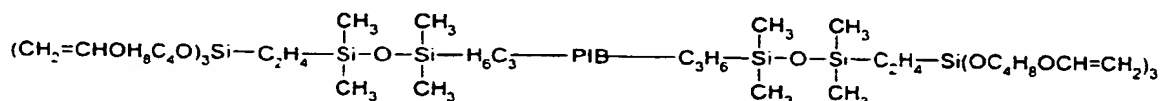
[0058] Cure Studies: The formulations were mixed in a Hauschild mixer by placing the desired amounts of components as noted in the examples. The cure study was performed on either a Fusion curing processor (300 or 600 watt lamps) or differential photocalorimeter (DPC) equipment. In the Fusion curing processor, the coating was applied on to a glass slide and by a roll coater or manually. The glass slide was conveyed through the Fusion curing processor at a fixed line speed, and cure energy was controlled by adjusting belt speeds. An IL 1350 radiometer/photometer (from International Lights) was used to monitor the ultraviolet light flux at the sample. The extent of cure was measured by observing surface tack (dry to touch) immediately after ultraviolet light curing. Through cure was evaluated by removing the cured film from substrate and evaluating tack at the bottom. Film thickness was measured by a micrometer. The DPC studies were conducted on a 930 model DPC (DuPont Instruments) and a model 910 differential scanning calorimeter (DuPont Instruments) equipped with a Fusion 300 watt Lamp. All DPC measurements were made in air. In all cases a radiometer was used to obtain the cure energy. Samples were radiated in-situ at 25°C. in air. The DPC data was analyzed using V4.1A DuPont 21000 software. DPC induction times were measured from first exposure to 1% conversion.

Example 1

[0059] The methoxysilyl-functional polyisobutylene polymers were prepared per the procedure disclosed by Saam et. al. in Example 2 of U.S. Patent 4,808,664, except that the starting polyisobutylene polymer was the commercially available Epion™ 200A (an allyl telechelic polyisobutylene made by Kaneka Corporation, Tokyo, Japan).

Example 2

[0060] A mixture of 1112 g of the polymer from Example 1 and 1500 ml of cyclohexane was added to a round bottom flask, equipped with mechanical stirrer, Dean-Stark separator and reflux condenser. To the flask was added 140 grams of 4-hydroxybutyl vinyl ether (HO(CH₂)₄OCH=CH₂) and 0.5 ml of tetraisopropyl titanate. The reaction mixture was heated at a temperature of 70°C. with stirring for eight hours, during which time approximately 35 ml of methanol was removed from the Dean-Stark separator. ¹H NMR spectrum of a small sample confirmed that the product had the following structure:

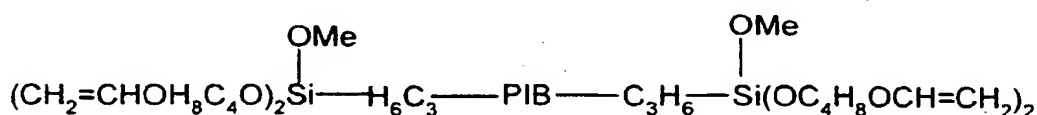


(Note: PIB denotes the initial polyisobutylene polymer)

[0061] The cyclohexane solvent was removed with a thin film stripper. Molecular weight data: $M_n = 6800$; M_w 10400; $M_w/M_n = 1.52$. This polymer is hereinafter referred to as POLYMER A.

Example 3

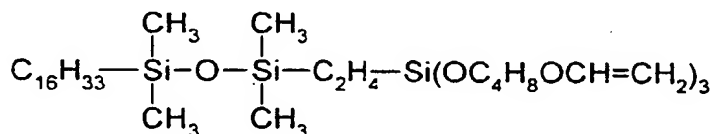
[0062] 50 grams of Epion™ 200A was dissolved 150 ml of heptane. Platinum (vinylsiloxane) catalyst was added to the mixture at a molar ratio of 1×10^{-4} equivalents/allyl group and 1.10 (equivalents per allyl group) of trichlorosilane was added dropwise to the reaction mixture. The reaction mixture was maintained for eight hours at 70°C. Proton nuclear magnetic resonance spectra confirmed the absence of allyl resonances. After cooling to room temperature, 40 ml of methylene chloride was added to the flask followed by 15 g of triethylamine. Thereafter, 15 ml of 4-hydroxybutyl vinyl ether was added dropwise from an addition funnel to the flask and after addition the contents were allowed to stir overnight. The precipitated salts were filtered off. The polymer was isolated by precipitation into methanol and dried. H^1 NMR spectra of the product confirms the following structure:



Molecular Weight data: $M_n = 7528$, $M_w = 35420$; $M_w/M_n = 4.70$. This polymer is hereinafter referred to as POLYMER B.

Example 4

[0063] 150 g of 1-hexadecene, 250 ml of cyclohexane and platinum (vinylsiloxane) catalyst at a molar ratio of 1×10^{-5} (equivalents/ C=C) were added to a round bottom flask equipped with a magnetic stirrer, reflux condenser, addition funnel and thermometer. Next, 186 grams of a siloxane having the formula $(\text{MeO})_3\text{Si}-\text{CH}_2-\text{CH}_2-(\text{Me}_2\text{SiOSi}(\text{Me}_2)\text{H})$ (disclosed in U.S. Patent 4,808,664), wherein Me hereinafter denotes a methyl group, was added slowly over a period of 30 minutes. The reaction was continued for 70°C. for two hours. GC analysis showed complete conversion. The reactor was evacuated (20 Torr) to strip off excess olefins. At this time, 235 g of 4-hydroxybutyl vinyl ether and Tzoz® TPT catalyst (from Dupont) at a molar ratio of 5×10^{-4} (equivalents/ C=C) were added to the pot and a Dean stark separator was added to the apparatus. After 5-6 hours of reflux, approximately 60 ml of methanol was recovered from dean-stark separator. GC analysis showed approximately 90% conversion. H^1 NMR data indicated the following structure:



This sample is referred to as Liquid A.

Example 5

[0064] Three formulations containing polymer A, liquid A, a 60/40 weight to weight mixture of tolyl (dodecylphenyl) iodonium trifluoromethanesulfonate diluted in dodecylphenol (hereinafter denoted "triflate catalyst"), a cationic photoinitiator and Darocur® 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one from Ciba Geigy, Terrytown, N.Y.), a free radical photoinitiator, were prepared by mixing these ingredients together in the amounts shown in Table 1.

Table 1

Sample	Liquid A (wt %)	Polymer A (wt %)	Triflate catalyst (wt %)	Darocur®1173 (wt %)
A	38	60	2	-
B	38	58	4	-

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Table 1 (continued)

Sample	Liquid A (wt %)	Polymer A (wt %)	Triflate catalyst (wt %)	Darocur®1173 (wt %)
C	38	58	2	2

[0065] The samples were tested in a DPC apparatus at 25°C. in air at 1.10 (Joules/cm²) cure energy. The analysis results of the DPC exotherm is reported in Table 2 below.

Table 2

Sample	Cure Energy (J/cm ²)	Cure Rate (W/g/min.)	Induction Time (s)	Peak Max. (s)	Thickness (mm)
A	1.11	3.94	11	43	0.35
B	1.11	5.96	10	36	0.60
C	1.11	52.76	4	14	0.90

[0066] The results show faster cure rate for ultraviolet cure of Sample C which contained both a free radical photoinitiator (such as Darocur® 1173) and cationic photoinitiator (such as the triflate catalyst) as compared with those which contained a cationic photoinitiator alone in formulations A and B. It is to be noted that the free radical photoinitiator alone will not provide ultraviolet cure of the composition. The preferred catalyst combination reduces the amount of cationic photocatalyst required in the formulation with faster ultraviolet cure rates. The faster ultraviolet cure rates are not possible by increased amounts of the cationic photoinitiator alone.

Example 6

[0067] Three formulations containing polymer A, liquid A, Darocur® 1173 and a mixture of bis(4-dodecylphenyl) iodonium hexafluoroantimonate (30-60 weight percent), C₁₂₋₁₄ alkylglycidyl ethers (30-60 weight percent), linear alkylate dodecylbenzene (5-10 weight percent), 2-isopropylthioxanthone (1-5 weight percent) (hereinafter the mixture is denoted as "antimonate catalyst"), were prepared by mixing these ingredients together in the amounts shown in Table 3.

Table 3

Sample	Liquid A (wt %)	Polymer A (wt %)	Antimonate catalyst (wt %)	Darocur®1173 (wt %)
D	38	60	2	-
E	38	58	4	-
F	38	58	2	2

[0068] The samples were tested in a DPC apparatus at 25°C. in air at 1.10 (Joules/cm²) cure energy. The analysis results of the DPC exotherm is reported in Table 4 below.

Table 4

Sample	Cure Energy (J/cm ²)	Cure Rate (W/g/min.)	Induction Time (s)	Peak Max. (s)	Thickness (mm)
D	1.11	23.05	10	32	0.95
E	1.11	30.08	7	27	0.85
F	1.11	63.75	4	14	1.20

[0069] The DPC results for Sample F in Table 3 as compared to Samples D and E showed that Sample F had a faster reaction rate than Samples D and E.

Example 7

[0070] The following example shows that formulation of the composition can be varied to achieve a similar effect. In this formulation, the liquid A is replaced with trimethylolpropane trivinyl ether (TMPTVE) and Polymer A is replaced with the polymer B. The formulations and DPC results are shown in Tables 5 and 6.

Table 5

Sample	Polymer B (wt%)	TMPTVE (wt%)	Triflate catalyst (wt%)	Darocur® 1173 (wt%)
G	59.0	38.0	3.0	-
H	58.0	38.0	2.0	2.0

Table 6

Sample	Cure Energy (mJ/cm ²)	Induction Time (s)	Enthalpy (J/g)	Peak Max. (s)
G	620	6.2	145	20
H	100	4.4	180	18

[0071] At a lower cure energy of 100 mJ/cm², the DPC exotherm for formulation H is similar to the formulation G, a DPC exotherm at 620 mJ/cm². The mixed catalyst provides a faster UV cure rates.

Example 8

[0072] Formulations shown in Table 7 were coated onto glass slides at approximately 2-4 micron thickness. A cure study was performed on a Fusion curing processor (300 Watt lamps), at a fixed line speed and cure energy was controlled by adjusting belt speeds. The minimum cure energy required for achieving a tack free surface was determined and the results are shown in Table 8.

Table 7

Sample	Liquid A (wt%)	Polymer A (wt%)	Triflate catalyst (wt%)	Antimonate catalyst (wt%)	Darocur®11 73 (wt %)
I	38	58	4	-	-
J	38	58	2	-	2
K	38	58	-	4	-
L	38	58	-	2	2

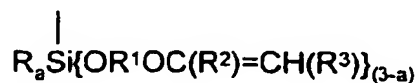
Table 8

Sample	Cure Energy (mJ/cm ²)	Line speed (ft/min.)
I	350	90
J	88	290
K	200	150
L	88	290

Claims

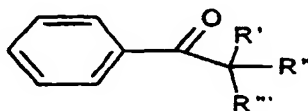
1. A radiation curable composition comprising:

(A) an alkenyl ether-functional polyisobutylene polymer in which at least 50 mole percent of the non-terminal repeating units of the polymer are isobutylene units and containing at least one group having the formula



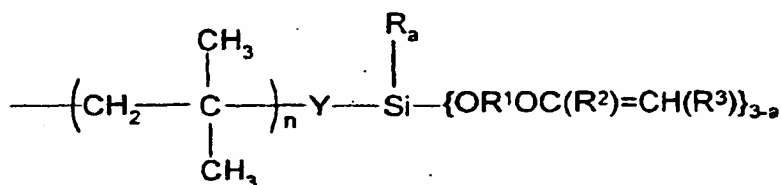
wherein R is independently selected from monovalent hydrocarbon groups and alkoxy groups, R¹ is a divalent hydrocarbon group having from 2 to 20 carbon atoms, R² and R³ are independently selected from a hydrogen atom or a monovalent hydrocarbon group and a has a value of 0 to 2;

(B) a cationic photoinitiator selected from onium salts, diaryliodonium salts of sulfonic acids, triarylsulfonium salts of sulfonic acids, diaryliodonium salts of boronic acids and triarylsulfonium salts of boronic acids; and
(C) a free radical photoinitiator having the formula

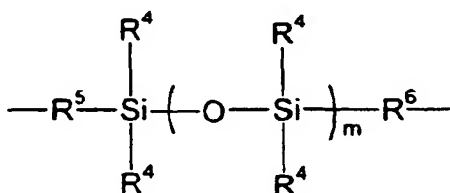


wherein R' is selected from a hydrogen atom, an alkoxy group or a halogen atom, R'' is selected from a hydroxy group, an alkoxy group and a halogen atom and R''' is selected from a hydrogen atom, an alkyl group or a halogen atom.

2. A composition according to claim 1 wherein (A) is a polymer containing at least one group having the formula



wherein at least 50 mole percent of the non-terminal repeating units of the polymer are isobutylene units, R, R¹, R², R³ and a are as defined in claim 1, n has a value from 5 to 10,000, and Y is selected from (i) an alkylene group having from 2 to 10 carbon atoms and (ii) a group having the formula

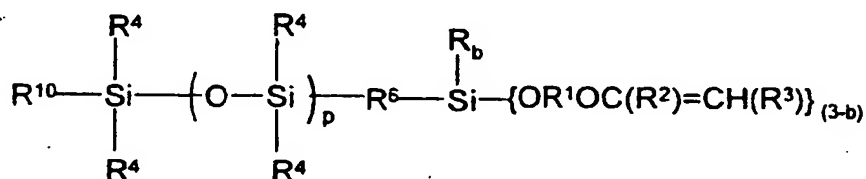


where R⁴ is a monovalent hydrocarbon group, R⁵ and R⁶ are independently alkylene groups having from 2 to 10 carbon atoms and m is an integer having a value from 1 to 5.

3. A composition according to claim 2 wherein R is independently selected from methyl or methoxy, R¹ is butylene, R² and R³ are hydrogen atoms, a has a value of 0 or 1, R⁴ is methyl, R⁵ is propylene, R⁶ is ethylene, m has a value of 1 and Y(i) is selected from ethylene, propylene, butylene, pentylene, trimethylene, 2-methyltrimethylene, pentamethylene, hexamethylene, 3-ethyl-hexamethylene, octamethylene and decamethylene.
4. A composition according to any of claims 1 to 3, wherein the composition further comprises (D) an alkenyl ether compound which is free of isobutylene units selected from

(i) a vinyl ether compound having the formula $(\text{CH}_2=\text{CHOR}^8)_d\text{CR}^9_{4-d}$ wherein R^8 is a divalent hydrocarbon group having from 1 to 20 carbon atoms, R^9 is hydrogen or a monovalent hydrocarbon group having from 1 to 20 carbon atoms and d has a value of 1 to 3,

(ii) a hydrocarbon silicone alkenyl ether compound having the formula



wherein R^1 and R^6 are independently divalent hydrocarbon groups having from 1 to 20 carbon atoms, R^4 is a monovalent hydrocarbon group having from 1 to 20 carbon atoms, R^2 and R^3 are independently selected from a hydrogen atom and a monovalent hydrocarbon group, R^{10} is an alkyl group having from 8 to 16 carbon atoms, R is independently selected from R^4 or an alkoxy group, b has a value of 0 to 2 and p has a value of 0 to 1, or

(iii) a long chain hydrocarbon silicone alkenyl ether compound having the formula



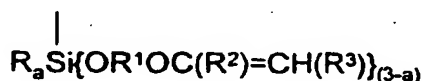
wherein R , R^1 , R^2 and R^3 are as defined in claim 1, R^{11} is an alkyl group having 8 to 16 carbon atoms and c has a value of 0 to 2.

5. A composition according to any of claims 1 to 4, wherein the composition further comprises (E) an alkylphenol having from 6 to 18 carbon atoms.

6. A method of making a radiation curable composition comprising:

(I) mixing

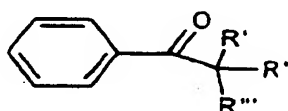
(A) an alkenyl ether-functional polyisobutylene polymer in which at least 50 mole percent of the non-terminal repeating units of the polymer are isobutylene units and containing at least one group having the formula



wherein R , R^1 , R^2 , R^3 and a are as defined in claim 1;

(B) a cationic photoinitiator selected from onium salts, diaryliodonium salts of sulfonic acids, triarylsulfonium salts of sulfonic acids, diaryliodonium salts of boronic acids and triarylsulfonium salts of boronic acids; and

(C) a free radical photoinitiator having the formula

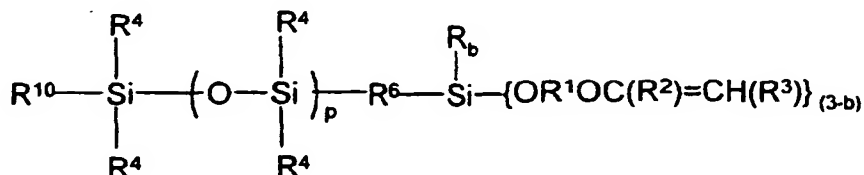


wherein R', R'' and R''' are as defined in claim 1.

7. A method of making an article of manufacture comprising:

- (I) applying a radiation curable composition as claimed in any of claims 1 to 6 to a solid substrate to form a coating; and
 (II) exposing the coating to an energy source selected from the group consisting of (i) ultraviolet light and (ii) visible light in an amount sufficient to cure the coating.

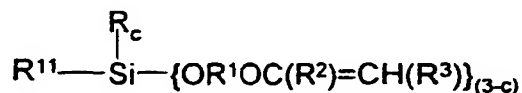
8. A hydrocarbon silicone alkenyl ether compound having the formula



wherein R¹ and R⁶ are divalent hydrocarbon groups having from 1 to 20 carbon atoms, R⁴ is a monovalent hydrocarbon group having from 1 to 20 carbon atoms, R¹⁰ is an alkyl group having from 8 to 16 carbon atoms, R² and R³ are independently selected from a hydrogen atom and a monovalent hydrocarbon group, R is independently selected from R⁴ and an alkoxy group, b has a value of 0 to 2 and p has a value of 0 to 1.

9. A compound according to claim 8 wherein R¹ is butylene, R⁶ is ethylene, R⁴ is methyl, R² and R³ are each hydrogen atoms, R¹⁰ is dodecyl or hexadecyl, R is independently methyl or methoxy, b has a value of 0 and p has a value of 1.

10. A hydrocarbon silicone alkenyl ether compound having the formula



wherein R is independently selected from monovalent hydrocarbon groups having from 1 to 20 carbon atoms and alkoxy groups, R² and R³ are independently a hydrogen atom or a monovalent hydrocarbon group, R¹¹ is an alkyl group having from 8 to 16 carbon atoms, R¹ is a divalent hydrocarbon group having 1 to 20 carbon atom and c has a value of 0 to 2.

11. A compound according to claim 10, wherein R¹ is butylene, R² and R³ are each hydrogen atoms, R is independently methyl or methoxy, R¹¹ is dodecyl or hexadecyl and c has a value of 0.



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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 9151

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 3 781 251 A (HERMES M) 25 December 1973 (1973-12-25) * claim 1 *	8-11	C08F290/04 C08F30/08 C08F8/00 C07F7/18
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The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7) C08F C07F
Place of search THE HAGUE		Date of completion of the search 28 March 2000	Examiner Meulemans, R
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28-03-2000

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